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Quantitative Assessment of Organic and Inorganic Contaminants in Charcoal

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Abstract: Thirty-one batches of commercial charcoal from various regions of Poland and Germany were tested for the presence of 20 toxic elements and polycyclic aromatic hydrocarbons (PAHs) using gas chromatography-mass spectrometry (GC-MS). Elements that are toxic to living organisms were determined using atomic absorption spectroscopy (AAS). They were classified as elements representing a very high degree of hazard (As, Cd, Cu, Hg, and Pb), high degree of hazard (Zn, Ba, Cr, Mn, and Mo), moderate degree of hazard (Co, Ni, Sn, and Te), and a low degree of hazard for living organisms and the environment (Ag, Bi, Ce, Se, Sr, and Zr). In regard to the most toxic elements, the highest concentration in the whole tested material was recorded for Cu. In addition, considerable amounts of Ba, Mn, and Sr, i.e., elements representing a high or moderate degree of hazard, were found in the tested charcoals. Moreover, all charcoals contained a wide range of PAHs, from naphthalene to benzo(ghi)perylene, with concentrations in a range between 12.55 and 3554.11 ng/g charcoal. In total, 25 unsubstituted PAHs were identified in the charcoal extracts. PAHs distributions were dominated by five-ring PAHs. The results indicate high carcinogenicity with ∑PAHcarc/∑PAHtot close to 1, as well as high TEQ and MEQ values. Thus, prolonged exposure to charcoal and charcoal dust might cause serious health problems. This applies to employees actively involved in the production and transport of charcoal and, to a lesser extent, users of this fuel.

Keywords: charcoal; grilling fuel; toxic elements; PAHs; carcinogens; GC-MS

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1. Introduction

Charcoal has been used since at least 50,000 years B.C., which is confirmed by the study of wood tar used to attach stone points to spears. This indicates the first conscious attempts to produce charcoal using the backfill method, i.e., through a partial dry wood distillation process under the earth cover, limiting oxygen access. In this way, small amounts of tar, an excellent adhesive and preservative product, were obtained as a byproduct [1]. The use of high temperatures for meat processing resulted in a more digestible diet and more extended storage of processed food [2]. The demand for charcoal production increased in the Bronze and Iron Ages when it facilitated everyday metal object and weapon production. The addition of carbon to iron during the smelting of ore in charcoal-fired furnaces became the basis of modern civilization [3]. At the end of the nineteenth century, the industry gradually moved away from charcoal towards fossil fuels and petroleum components. The renaissance of charcoal as fuel in its original form occurred in the 1940s. Grill grates for meat hung over a fire on a semicircular bowl filled with fuel (charcoal) were quickly adopted worldwide [4]. Grilling has become a favorite form of food preparation during family gatherings and outdoor activities.

In the 1980s, researchers focused on the quality and possible harmfulness of grilled food, e.g., carcinogenic substances in grilled meat [5–7]. Polycyclic aromatic hydrocarbons (PAHs) primarily come from the thermal treatment of meat (fat and meat grilled directly over a heated surface) and gaseous emissions from charcoal combustion. Medical observations confirmed that PAHs contribute to many civilization and occupational diseases

in modern society [8]. Whereas there are extensive studies on PAHs in biochar used as adsorbents of soil contaminants, grill fuel is not considered a significant source of these compounds, despite that both biochar and charcoal are produced in the pyrolysis of plant material [9–11]. It is well known that thermal decomposition of organic material leads to the production of tar being a complex mixture of PAHs of different condensation stages, phenolic compounds, and other oxygenated compounds when the process is carried out in an oxygen-depteted condition [12]. Moreover, these compounds are formed during every incomplete combustion process, whether biomass or fossil fuels are combusted [13,14]. These compounds are the object of extensive research due to their muta- and carcinogenic properties [15,16].

Exposure to fuels used for heat food treatment, such as charcoal, can pose many risks, not limited to charcoal combustion as a barbecue fuel. Risks may arise when producing, pouring, packing, transporting, and storing barbecue fuels characterized by low density, which promotes their easy crushing and dusting [17–19]. Employees in production plants and broadly defined consumers, both adults and children, are exposed to fine charcoal dust emissions. Knowledge of carcinogenic compounds and selected harmful chemical element contents in grill fuels is as important as their combustion on people, food products, and the environment.

The research presented here aims to assess PAH and carcinogenic element concentrations in charcoals intended for grill devices. To our knowledge, charcoal used for cooking has not been examined on a large scale for the presence of these components. Researchers have mainly focused on analyzing thermally processed food products or evaluating the gases emitted during charcoal combustion [17–20]. This study of grill fuels shows that harmful compounds are already present in the fuel itself. However, their contents vary from one fuel to another. Thus, it possible to limit charcoal users' exposure to these compounds by eliminating the most contaminated charcoals if their composition is known.

2. Materials and Methods

The individual charcoals were quartered, and then each fourth part of each sample was sent to the accredited laboratory, Bureau Veritas Commodities Canada Ltd. The analysis was performed in accordance with the applied methodology specified under the analytical codes MA250 and AQ200. The concentrations of the following elements were determined (elements listed in order of increasing atomic weight):

Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Zr, Mo, Ag, Cd, Sn, Te, Ba, Ce, Hg, Pb, and Bi.

The listed elements were selected on the basis of their toxicity being very high, high, medium, and low [21–23]. The division is based on living organisms' response to selected toxic element doses. Their limit values were determined on the basis of PN-EN ISO 17225-1:2014-0710 [24], PN-EN ISO 16967:2015-0611 [25], and "Hazardous substance fact sheet" [26] and are presented in Table 1.

Table 1. Limit values of toxic elements in solid fuels calculated from [21–26].

Symbol	Cr	Mn	Co	Ni	Cu	Zn	As	Se	Sr	Zr	Mo	Ag	Cd	Sn	Te	Ba	Ce	Hg	Pb	Bi
ppm	1.0	83.0	1.5	0.5	2.0	10.0	0.2	0.3	5.0	0.5	24.0	20.0	0.1	0.1	1.0	10.0	10.0	0.02	2.0	0.1
σ	4.9	121.5	0.85	4.95	4.75	47.5	0.95	3.82	-	-	40	3	0.22	0.1	11.5	10.5	-	0.02	4.75	2.49

σ—standard deviation.

Charcoal was purchased in original commercial packaging with a net unit weight of 2500 g, partially directly from grill fuel producers as a part of a cooperation, and partially bought in supermarkets. Altogether, 31 different charcoals were obtained for the research aims. Charcoal samples were classified according to the method of obtaining material for the research and production method and the location of production. The type of wood used for the production of charcoal was also declared by the grill fuel producers (Table 2).

Table 2. Production method (column 2—wood is burnt with low airflow in retorts, column 3—wood is annealed under controlled conditions, usually using modern automated production lines, column 4—wood is burnt in an earth pit by arranging wooden logs on burning branches and covering the pit with excavated earth to cut off the air supply [27]), production location, and type of wood used to produce charcoal.

Sample	Production Method			Location Country/Voivodeship or Region	Type of Wood Used for the Production
	Generator	Annealed	Earth Pits		
1	2	3	4	5	6
W1	X			Poland /West Pomeranian Voivodeship	hornbeam, beech, ash
W2		X		Poland/West Pomeranian Voivodeship	beech, birch
W3		X		Poland/Lublin Voivodeship	hornbeam, beech, ash, oak
W4				no data	
W5		X		Poland/Podlaskie Voivodeship	beech
W6				no data	
W7	X			Poland/Podlaskie Voivodeship	hornbeam, beech, ash, oak
W8		X		Poland/Mazovian Voivodeship	hornbeam, beech, ash, oak
W9			X	Poland/Podlaskie Voivodeship	beech, oak
W10		X		Poland/Podlaskie Voivodeship	beech
W11		X		Poland/Greater Poland Voivodeship	beech, oak, ash, hornbeam,
W12		X		Poland/Lesser Poland	beech, hornbeam, oak, birch
W13				no data	
W14			X	Poland/Podkarpackie Voivodeship	beech, hornbeam
W15	X			Poland/Greater Poland Voivodeship	birch, hornbeam, oak, beech
W16	X			Poland/West Pomeranian Voivodeship	hornbeam, beech, ash, oak
W17				no data	
W18		X		Poland/West Pomeranian Voivodeship	beech, ash
W19	X			Poland/Greater Poland Voivodeship	beech, hornbeam, oak, birch
W20		X		Poland/Mazovian Voivodeship	no data
W21		x		Poland/Lesser Poland	beech, hornbeam, oak, birch
W22		X		Poland/Greater Poland Voivodeship	beech, hornbeam, oak, birch
W23		X		Poland/Mazovian Voivodeship	mixed deciduous wood
W24	X			Poland/Kuyavian-Pomeranian Voivodeship	mixed deciduous wood
W25		X		Poland/Silesian Voivodeship	beech, hornbeam, birch
W26		X		Poland/Mazovian Voivodeship	beech, hornbeam, oak, birch
W27		X		Poland/Kuyavian-Pomeranian Voivodeship	no data
W28		X		Poland/Pomeranian Voivodeship	beech, hornbeam, oak, birch
W29		X		Germany/Mannheim	beech, hornbeam, oak, birch
W30		X		Poland/Lesser Poland	hornbeam, birch
W31		X		Poland/Lower Silesian Voivodeship	beech, hornbeam, oak, birch

The charcoal was ground (from each package separately) to a fraction of 1–0.5 mm. After averaging from the material obtained in this way, samples weighing 4 g–7 g were taken. Each of the samples was subjected to extraction in the Dionex ASE 350 extractor dedicated for rapid extraction under pressure. The method has been selected as it allows recovery of PAHs 2x higher than commonly applied Soxhlet extraction [28]. The extracts were evaporated at room temperature and weighed. Extraction yields are shown in Table 3. The obtained extracts were derivatized to obtain derivatives with properties enabling their determination using the applied analytical method. To each extract obtained from the samples, 100 µL of NO-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and 10 µL of pyridine were added. Then, the solution was reconstituted to 1 mL with hexane. The prepared solutions were placed in a laboratory oven for 3 h at 70 °C. After removing the extracts from the oven, any fluid losses from individual vials were reconstituted to 1 mL with a solvent (hexane).

The derivatized charcoal extracts were analyzed with an Agilent 7890A (Agilent, Santa Clara, CA, USA) gas chromatograph equipped with an HP-35 column coated with a 0.25 µm stationary phase film coupled with an Agilent Technology 5975C XL MDS mass spectrometer (Agilent, Santa Clara, CA, USA). The experimental conditions were as follows: carrier gas—He; temperature—50 °C (isothermal for 2 min); heating rate—up to 175 °C at 10 °C/min, to 225 °C at 6 °C/min and, finally, to 300 °C at 4 °C/min. The final temperature (300 °C) was held for 20 min. The mass spectrometer was operated in ionization mode (70 eV, full scan) and scanned from 50–650 Da. The compounds were identified by their mass spectra and comparison of peak retention times with those of standard compounds. The data were processed using Hewlett-Packard Chemstation software. Peaks were integrated manually. The quantitative analysis was performed based on the 5-point calibration curves for the analytical standards. Calculations were based

on average values of integrated peak areas from three repetitions of GC-MS analyses of the standards as well as the charcoal extracts. All standard purities were checked prior to calibration curve preparation under the same analytical conditions as those used for the extract analyses. The derivatizing reagents, stock solutions, and calibration solutions containing the analytes were stored in the absence of light and under refrigeration at 5 °C.

Table 3. Summary of the elemental content of the tested charcoals.

Sample / ppm	Symbol																			
	Cr	**Mn**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Sr**	**Zr**	**Mo**	**Ag**	**Cd**	**Sn**	**Te**	**Ba**	**Ce**	**Hg**	**Pb**	**Bi**
W1	1	32.0	0.3	0.9	4.5	7.6	<0.2	0.4	260	0.3	1.24	<0.02	0.02	<0.1	0.88	98	1.73	<0.01	1.58	<0.04
W2	<1	124.0	0.2	5.0	3.8	7.7	<0.2	<0.3	47	1.0	0.24	<0.02	0.02	<0.1	0.20	96	0.29	<0.01	0.36	<0.04
W3	<1	240.0	0.2	2.0	4.0	6.0	<0.2	<0.3	25	0.4	0.10	<0.02	0.02	<0.1	0.16	157	0.10	<0.01	0.26	<0.04
W4	1	218.0	0.2	4.8	4.1	31.8	0.2	0.3	91	0.6	0.08	0.02	0.09	<0.1	0.30	125	0.06	0.02	0.92	<0.04
W5	<1	717.0	0.2	3.1	5.8	6.6	<0.2	<0.3	18	<0.2	0.09	0.24	0.03	<0.1	0.09	57	0.13	<0.01	0.27	<0.04
W6	1	231.0	0.2	4.6	4.2	26.0	<0.2	<0.3	83	0.4	0.08	<0.02	0.07	<0.1	0.18	109	0.09	<0.01	0.81	<0.04
W7	<1	273.0	0.2	1.8	3.7	8.4	0.3	<0.3	32	<0.2	0.06	0.33	0.05	<0.1	0.13	125	0.08	<0.01	0.38	<0.04
W8	<1	127.0	<0.2	0.6	7.0	47.3	<0.2	<0.3	17	0.5	0.07	0.82	0.20	<0.1	0.05	44	0.06	<0.01	1.50	<0.04
W9	<1	220.0	<0.2	1.0	4.0	8.0	0.3	<0.3	127	0.6	0.81	<0.02	0.09	<0.1	0.58	129	0.59	<0.01	0.69	<0.04
W10	<1	1817.0	0.5	1.0	3.4	41.9	0.3	<0.3	27	0.3	0.05	<0.02	0.23	<0.1	0.11	97	0.08	<0.01	1.98	<0.04
W11	<1	127.0	<0.2	0.5	4.0	4.5	<0.2	<0.3	10	<0.2	0.05	<0.02	0.03	<0.1	0.12	44	0.03	<0.01	0.36	<0.04
W12	<1	366.0	<0.2	1.0	3.5	23.1	0.2	<0.3	16	0.2	0.09	0.34	0.09	<0.1	0.18	47	0.18	<0.01	1.65	<0.04
W13	<1	183.0	0.2	0.9	2.4	11.3	0.2	<0.3	47	<0.2	0.09	<0.02	0.09	<0.1	0.29	63	0.09	<0.01	2.0	<0.04
W14	<1	76.0	<0.2	1.5	5.1	3.5	<0.2	<0.3	34	0.2	0.05	<0.02	0.04	<0.1	0.20	37	0.09	<0.01	0.23	<0.04
W15	<1	272.0	0.4	2.4	3.7	9.0	<0.2	<0.3	44	<0.2	0.07	0.21	0.04	<0.1	0.14	46	0.17	<0.01	0.36	<0.04
W16	<1	293.0	0.2	1.5	4.5	60.2	0.5	<0.3	25	<0.2	0.05	<0.02	0.02	<0.1	0.12	79	0.11	<0.01	0.65	<0.04
W17	<1	169.0	<0.2	1.5	2.9	21.6	<0.2	0.3	8	0.3	0.09	<0.02	0.15	<0.1	0.16	71	0.93	<0.01	0.97	<0.04
W18	<1	8.0	<0.2	0.3	2.7	9.6	<0.2	<0.3	53	0.2	0.05	<0.02	0.02	<0.1	0.10	4	0.02	<0.01	0.19	<0.04
W19	<1	179.0	<0.2	0.8	3.3	15.3	<0.2	<0.3	38	<0.2	0.15	<0.02	0.04	<0.1	0.14	45	0.10	<0.01	0.24	<0.04
W20	<1	145.0	<0.2	1.7	4.8	5.4	<0.2	<0.3	14	0.2	0.05	<0.02	0.08	<0.1	0.10	51	0.06	<0.01	0.31	<0.04
W21	<1	50.0	<0.2	0.7	4.2	4.9	0.3	<0.3	65	<0.2	0.12	<0.02	0.05	<0.1	0.16	15	0.05	<0.01	0.23	<0.04
W22	<1	338.0	0.4	1.2	6.5	53.2	<0.2	<0.3	54	<0.2	0.13	<0.02	0.03	<0.1	0.33	68	0.20	<0.01	0.46	<0.04
W23	<1	349.0	<0.2	1.7	4.0	8.4	<0.2	0.4	37	<0.2	0.09	<0.02	0.03	<0.1	0.24	76	0.12	<0.01	0.29	<0.04
W24	<1	318.0	0.3	1.2	3.8	13.5	0.2	0.4	9	0.3	0.05	0.23	0.10	<0.1	0.05	41	0.19	<0.01	0.37	<0.04
W25	<1	28.0	<0.2	1.6	3.4	5.1	<0.2	<0.3	14	0.2	0.06	<0.02	0.03	<0.1	0.07	20	0.07	<0.01	0.16	<0.04
W26	<1	113.0	<0.2	1.1	3.3	4.2	0.3	<0.3	16	<0.2	0.05	<0.02	0.04	<0.1	0.10	21	0.10	<0.01	0.35	<0.04
W27	<1	359.0	<0.2	1.4	3.4	9.0	<0.2	0.3	25	<0.2	0.05	<0.02	0.06	<0.1	0.19	94	0.06	<0.01	0.41	<0.04
W28	<1	4.0	<0.2	0.4	1.5	3.7	<0.2	<0.3	16	<0.2	0.05	<0.02	0.03	<0.1	0.05	12	0.03	<0.01	0.13	<0.04
W29	<1	141.0	<0.2	1.9	3.9	4.8	<0.2	<0.3	17	<0.2	0.05	0.28	0.06	<0.1	0.09	41	0.11	<0.01	0.27	<0.04
W30	<1	117.0	0.3	1.0	3.4	41.9	<0.2	0.4	27	0.3	0.05	<0.02	0.13	<0.1	0.38	93	0.22	<0.01	1.98	<0.04
W31	<1	747.0	0.2	1.4	8.9	26.7	<0.2	0.4	175	0.4	0.39	0.21	0.03	<0.1	0.24	126	0.92	<0.01	1.46	<0.04
*** MDL**	1	1	0.2	0.1	0.1	0.2	0.2	0.3	1	0.2	0.05	0.02	0.02	0.1	0.05	1	0.02	0.01	0.02	0.04

* MDL—method detection limit (the detection limit).

The linear correlation between the peak areas and PAH concentrations was checked within the range of 0.10–10 µg/mL, with correlation coefficient values within the range of 0.997–0.998. For quality assurance and quality control (QA/QC), the analysis of each sample series was accompanied by the analysis of a blank sample comprising the whole analysis procedure to assess possible contamination. The method performance was verified by analyzing the NIST SRM 1649b reference material and comparing the results with the certified concentrations of the investigated PAHs. The standard recoveries ranged from 91% to 111%± 5%–19%. The limits of detection (LODs) were calculated as three times the standard deviation of background peaks in the procedural blanks repeated three times. Average LODs values were 2.0 ± 0.05 ng/mL. Concentrations below the LOD were considered zero for all calculations.

3. Results

A quantitative analysis of charcoal samples for the content of elements harmful to humans is shown in Table 3.

A high strontium concentration of 127 ppm, which is 25.4 times the limit value (5 ppm), was found in the W9 sample. High and very high concentrations of strontium were determined in the W31 (175 ppm) and W1 samples (260 ppm, which translates into 52 times the limit value for solid fuels). The lowest strontium concentrations were observed in the W17 (8 ppm) and W24 samples (9 ppm). The highest concentrations of copper were recorded in the W22 (6.5 ppm), W8 (7.0 ppm), and W31 (8.9 ppm) samples, while the limit value was 2 ppm. On average, copper concentrations in the tested charcoals ranged from 2.4 ppm to 4.8 ppm. The concentration of zinc, ranging from 13.5 ppm for the W24 sample to 50.2 ppm for the W16 sample, exceeded the limit value of 10 ppm in 13 samples

out of 31. The lowest zinc concentration (3.5 ppm) was found in the W14 sample. The concentration of Ba ranged from 12 to 157 ppm and exceeded the limit value of 10 ppm in all samples except for the W18 sample (4 ppm). The highest concentration of Ni was found in the W4 (4.8 ppm) and W2 (5 ppm) samples, which is 10 times the limit value (0.5 ppm). Twenty-six samples exceeded the recommended values from one to six times; in the case of three samples, namely, the W18 (0.3 ppm), W28 (0.4 ppm), and W11 (0.5 ppm) samples, the Ni concentration was within the recommended values. The highest concentrations of manganese were found in samples W5 (717.0 ppm) and W31 (747.0 ppm), reaching a record value in the W10 sample (1817.0 ppm). In the three samples, namely, W25, W1, and W14, the concentration of manganese ranged from 28.0 to 76.0, well below the limit value of 83.0 ppm. Trace amounts of Mn, from 4.0 to 8.0 ppm, were observed in the W28 and W18 samples. In the case of four samples, W30, W17, W8, and W10, cadmium, with concentrations ranging from 0.13 to 0.23 ppm, exceeded the limit value of 0.1 ppm. The concentration of Cd was below 0.1 ppm in the remaining 27 samples. In the W16 sample (0.5 ppm), a two- and a half-fold increase above the recommended arsenic level (0.2 ppm) was observed; in the case of the next five samples, namely, the W7, W9, W10, W21, and W26 samples, the As concentration was 1.5 times the limit value (0.2 ppm). In the remaining 25 samples, arsenic was found in trace amounts (below 0.2 ppm). In regard to Se, slight exceedances of the limit values (by 0.1 ppm) were observed in samples W1, W23, W24, and W30. In 30 samples, the mercury concentration was <0.01 ppm. Hg concentrations reached the reference range of 0.02 ppm only in the case of the W4 sample. The remaining elements in the tested material, including Ag, Mo, Cr, Co, Bi, Ce, Zn, and Te, were present in trace amounts. The total content of toxic elements is presented in Tables 4 and 5. For each of the element groups distinguished according to their toxicity, the charcoal samples were selected that show element concentration exceeding the limit values shown in Table 1. Figure 1 presents the examples of concentration for Cu, an element included in the group of the highest toxicity, Ba in the high-risk group, Ni being in the group of medium toxicity, and Zr showing a low risk to the environment.

Table 4. Summary of the elemental content of the tested toxic charcoals with a very high and high degree of potential hazard to the environment and the health of living organisms.

Sample / ppm	Symbol											
	As	Cd	Cu	Hg	Pb	Zn	Σ	Ba	Cr	Mn	Mo	Σ
W1	<0.2	0.02	4.5	<0.01	1.58	7.6	13.91	98	1	32.0	1.24	132.24
W2	<0.2	0.02	3.8	<0.01	0.36	7.7	12.09	96	<1	124.0	0.24	221.24
W3	<0.2	0.02	4.0	<0.01	0.26	6.0	26	157	<1	240.0	0.10	353.48
W4	0.2	0.09	4.1	0.02	0.92	31.8	37.13	125	1	218.0	0.08	344.08
W5	<0.2	0.03	5.8	<0.01	0.27	6.6	12.91	57	<1	717.0	0.09	775.09
W6	<0.2	0.07	4.2	<0.01	0.81	26.0	50.04	109	1	231.0	0.08	1119.17
W7	0.3	0.05	3.7	<0.01	0.38	8.4	12.84	125	<1	273.0	0.06	399.06
W8	<0.2	0.20	7.0	<0.01	1.50	47.3	56.21	44	<1	127.0	0.07	172.07
W9	0.3	0.09	4.0	<0.01	0.69	8.0	69.05	129	<1	220.0	0.81	571.13
W10	0.3	0.23	3.4	<0.01	1.98	41.9	47.82	97	<1	1817.0	0.05	1915.05
W11	<0.2	0.03	4.0	<0.01	0.36	4.5	9.1	44	<1	127.0	0.05	172.05
W12	0.2	0.09	3.5	<0.01	1.65	23.1	56.92	47	<1	366.0	0.09	2087.1
W13	0.2	0.09	2.4	<0.01	2.0	11.3	16	63	<1	183.0	0.09	247.09
W14	<0.2	0.04	5.1	<0.01	0.23	3.5	9.08	37	<1	76.0	0.05	114.05
W15	<0.2	0.04	3.7	<0.01	0.36	9.0	25.08	46	<1	272.0	0.07	361.14
W16	0.5	0.02	4.5	<0.01	0.65	60.2	65.88	79	<1	293.0	0.05	373.05
W17	<0.2	0.15	2.9	<0.01	0.97	21.6	25.83	71	<1	169.0	0.09	241.09
W18	<0.2	0.02	2.7	<0.01	0.19	9.6	91.71	4	<1	8.0	0.05	614.14
W19	<0.2	0.04	3.3	<0.01	0.24	15.3	19.09	45	<1	179.0	0.15	225.15
W20	<0.2	0.08	4.8	<0.01	0.31	5.4	10.8	51	<1	145.0	0.05	197.05
W21	0.3	0.05	4.2	<0.01	0.23	4.9	29.89	15	<1	50.0	0.12	422.2
W22	<0.2	0.03	6.5	<0.01	0.46	53.2	60.4	68	<1	338.0	0.13	407.13
W23	<0.2	0.03	4.0	<0.01	0.29	8.4	12.93	76	<1	349.0	0.09	426.09
W24	0.2	0.10	3.8	<0.01	0.37	13.5	73.33	41	<1	318.0	0.05	833.22
W25	<0.2	0.03	3.4	<0.01	0.16	5.1	8.9	20	<1	28.0	0.06	49.06
W26	0.3	0.04	3.3	<0.01	0.35	4.2	8.2	21	<1	113.0	0.05	135.05
W27	<0.2	0.06	3.4	<0.01	0.41	9.0	17.1	94	<1	359.0	0.05	184.11
W28	<0.2	0.03	1.5	<0.01	0.13	3.7	5.57	12	<1	4.0	0.05	17.05
W29	<0.2	0.06	3.9	<0.01	0.27	4.8	9.24	41	<1	141.0	0.05	183.05
W30	<0.2	0.13	3.4	<0.01	1.98	41.9	14.81	93	<1	117.0	0.05	200.1
W31	<0.2	0.03	8.9	<0.01	1.46	26.7	37.3	126	<1	747.0	0.39	874.39

Table 5. Summary of the elemental content of the tested toxic elements representing a medium degree of hazard to the environment and the health of living organisms.

Sample / ppm	Symbol											
	Co	**Ni**	**Sn**	**Te**	**Σ**	**Ag**	**Bi**	**Ce**	**Se**	**Sr**	**Zr**	**Σ**
W1	0.3	0.9	<0.1	0.88	2.18	<0.2	<0.04	1.73	0.4	260	0.3	48.83
W2	0.2	5.0	<0.1	0.20	5.5	<0.2	<0.04	0.29	<0.3	47	1.0	311.5
W3	0.2	2.0	<0.1	0.16	7.68	<0.2	<0.04	0.10	<0.3	25	0.4	92.2
W4	0.2	4.8	<0.1	0.30	5.4	0.2	<0.04	0.06	0.3	91	0.6	18.91
W5	0.2	3.1	<0.1	0.09	3.49	0.24	<0.04	0.13	<0.3	18	<0.2	111.11
W6	0.2	4.6	<0.1	0.18	8.89	<0.2	<0.04	0.09	<0.3	83	0.4	32.95
W7	0.2	1.8	<0.1	0.13	2.23	0.33	<0.04	0.08	<0.3	32	<0.2	18.72
W8	<0.2	0.6	<0.1	0.05	0.95	0.82	<0.04	0.06	<0.3	17	0.5	51.67
W9	<0.2	1.0	<0.1	0.58	3.18	<0.2	<0.04	0.59	<0.3	127	0.6	27.92
W10	0.5	1.0	<0.1	0.11	1.71	<0.2	<0.04	0.08	<0.3	27	0.3	10.77
W11	<0.2	0.5	<0.1	0.12	0.92	<0.2	<0.04	0.03	<0.3	10	<0.2	38.69
W12	<0.2	1.0	<0.1	0.18	2.63	0.34	<0.04	0.18	<0.3	16	0.2	47.83
W13	0.2	0.9	<0.1	0.29	1.49	<0.2	<0.04	0.09	<0.3	47	<0.2	34.83
W14	<0.2	1.5	<0.1	0.20	2	<0.2	<0.04	0.09	<0.3	34	0.2	82.66
W15	0.4	2.4	<0.1	0.14	3.49	0.21	<0.04	0.17	<0.3	44	<0.2	25.85
W16	0.2	1.5	<0.1	0.12	1.92	<0.2	<0.04	0.11	<0.3	25	<0.2	9.77
W17	<0.2	1.5	<0.1	0.16	1.96	<0.2	<0.04	0.93	0.3	8	0.3	35.62
W18	<0.2	0.3	<0.1	0.10	3.88	<0.2	<0.04	0.02	<0.3	53	0.2	38.84
W19	<0.2	0.8	<0.1	0.14	1.24	<0.2	<0.04	0.10	<0.3	38	<0.2	14.8
W20	<0.2	1.7	<0.1	0.10	2.1	<0.2	<0.04	0.06	<0.3	14	0.2	53.64
W21	<0.2	0.7	<0.1	0.16	3.34	<0.2	<0.04	0.05	<0.3	65	<0.2	54.94
W22	0.4	1.2	<0.1	0.33	2.03	<0.2	<0.04	0.20	<0.3	54	<0.2	37.96
W23	<0.2	1.7	<0.1	0.24	2.24	<0.2	<0.04	0.12	0.4	37	<0.2	92.9
W24	0.3	1.2	<0.1	0.05	4.27	0.23	<0.04	0.19	0.4	9	0.3	14.81
W25	<0.2	1.6	<0.1	0.07	1.97	<0.2	<0.04	0.07	<0.3	14	0.2	16.84
W26	<0.2	1.1	<0.1	0.10	1.5	<0.2	<0.04	0.10	<0.3	16	<0.2	31.65
W27	<0.2	1.4	<0.1	0.19	3.47	<0.2	<0.04	0.06	0.3	25	<0.2	16.77
W28	<0.2	0.4	<0.1	0.05	0.75	<0.2	<0.04	0.03	<0.3	16	<0.2	17.93
W29	<0.2	1.9	<0.1	0.09	2.29	0.28	<0.04	0.11	<0.3	17	<0.2	34.7
W30	0.3	1.0	<0.1	0.38	3.04	<0.2	<0.04	0.22	0.4	27	0.3	176.87
W31	0.2	1.4	<0.1	0.24	1.94	0.21	<0.04	0.92	0.3	175	0.4	262.67

The extract yields of the charcoals investigated varied in the range of 0.06–0.35% wt. The highest extract yields were found for the W14 (0.35% wt.) sample from the gravity method and the lowest for the W4 sample of an unknown production method (Table 2).

The investigated charcoal extracts were very rich in polycyclic aromatic hydrocarbons, both with respect to PAH concentrations and the number of compounds occurring. The following compounds were identified: naphthalene (N) (m/z = 128), biphenyl (B) (m/z = 154), acenaphthene (Ac) (m/z = 154), acenaphthylene (Ace) (m/z = 152), fluorene (F) (m/z = 166), phenanthrene (P) (m/z = 178), anthracene (A) (m/z = 178), methylenophenanthrene (MeP) (m/z = 190), fluoranthene (Fl) (m/z = 202), acenthrylene (Acen) (m/z = 202), acephenanthrylene (AceP) (m/z = 202), pyrene (Py) (m/z = 202), benzo(c)phenanthrene (B(c)P) (m/z = 228), benzo(a)anthracene (B(a)A) (m/z = 228), chrysene (Ch) (m/z = 228), benzo(ghi)fluoranthene (B(ghi)Fl) (m/z = 226), acepyrene (AcePy)(m/z = 226), benzofluoranthenes (BF) (m/z = 252), benzopyrenes (BP) (m/z = 252), perylene (Per) (m/z = 252), indeno (cd-1,2,3)pyrene (IP) (m/z = 276), and benzo(ghi)perylene (B(ghi)Per) (m/z = 276). The generalized PAH distribution is shown in Figure 2. Most unsubstituted PAHs were accompanied by alkyl C1-C3 derivatives. Phenalenes and PAHs heavier than six-ring compounds were not found in the charcoal extracts. The most numerous unsubstituted PAHs were in the W14 sample (25 identified compounds and the least numerous in the W11, W17, and W28 samples (11 identified compounds).

Generally, the highest concentrations in distribution were shown by the five-ring PAHs benzo(b)-and benzo(k)fluoranthenes, 91.70 and 31.21 ng/g (aver.), respectively; followed by benzo(a)pyrenes and benzo(e)pyrenes, 72.45 and 69.63 ng/g (aver.), respectively; and perylene, 14.98 ng/g (aver.). Lighter 2–3-ring PAHs were the minor charcoal extract components, most likely because they evaporated during wood pyrolysis (Figure 3).

Only naphthalene showed elevated contents in some of the samples, up to 50.20 ng/g (W6, W8, W10, and W13). Anthracene, considered to be a product of biomass/coal combustion [29], showed relatively low concentrations, 0.03–5.43 ng/g and 0.94 ng/g on average) compared to phenanthrene, 0.13–32.46 ng/g, 5.44 ng/g on average (Table 6). This is reflected by the P/A ratio being in the range from 2.98 (W17) to 13.95 (W6) (Table 7).

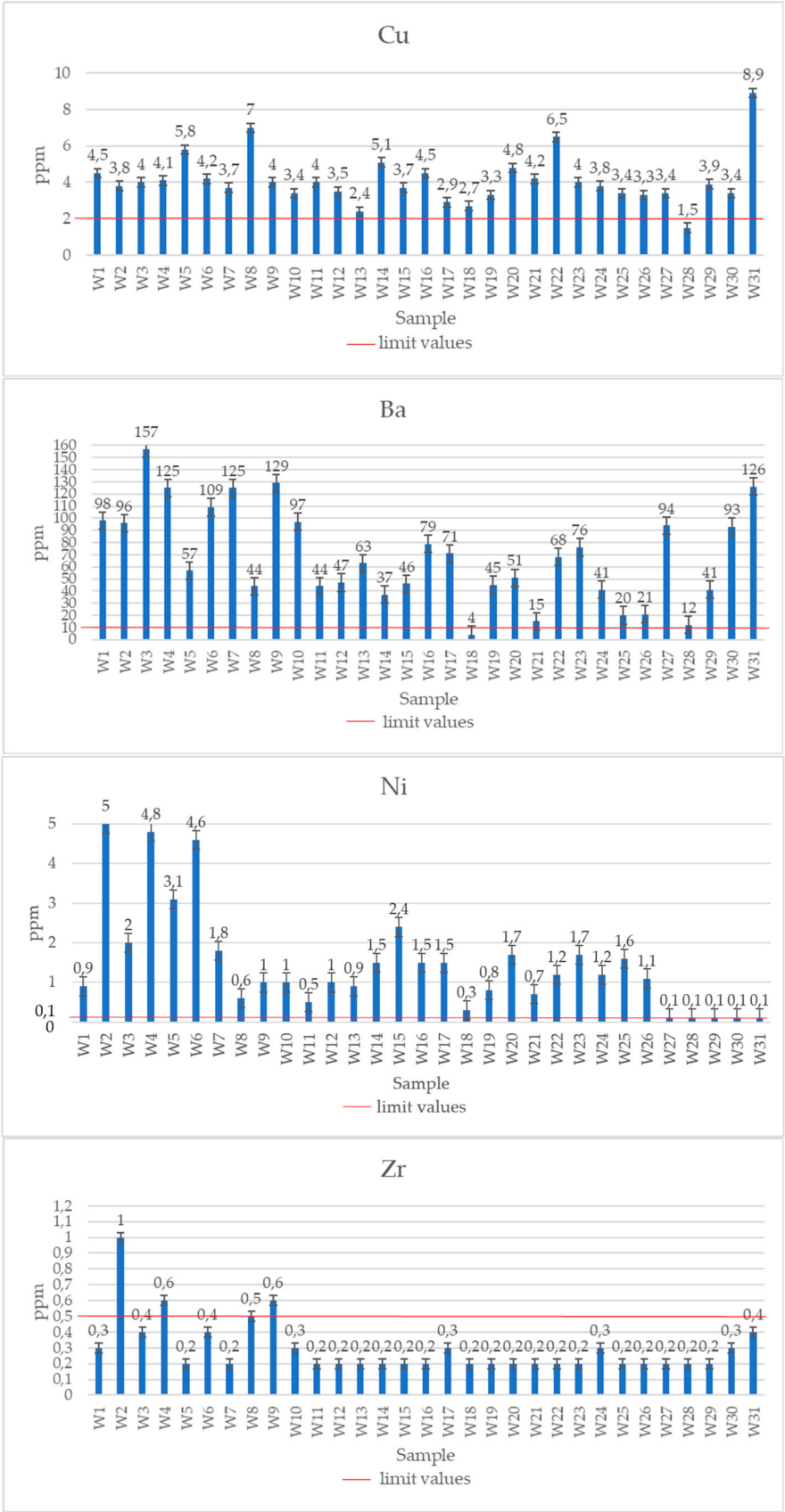

Figure 1. Examples of metal contents in the charcoals investigated; red line represents acceptable limit values.

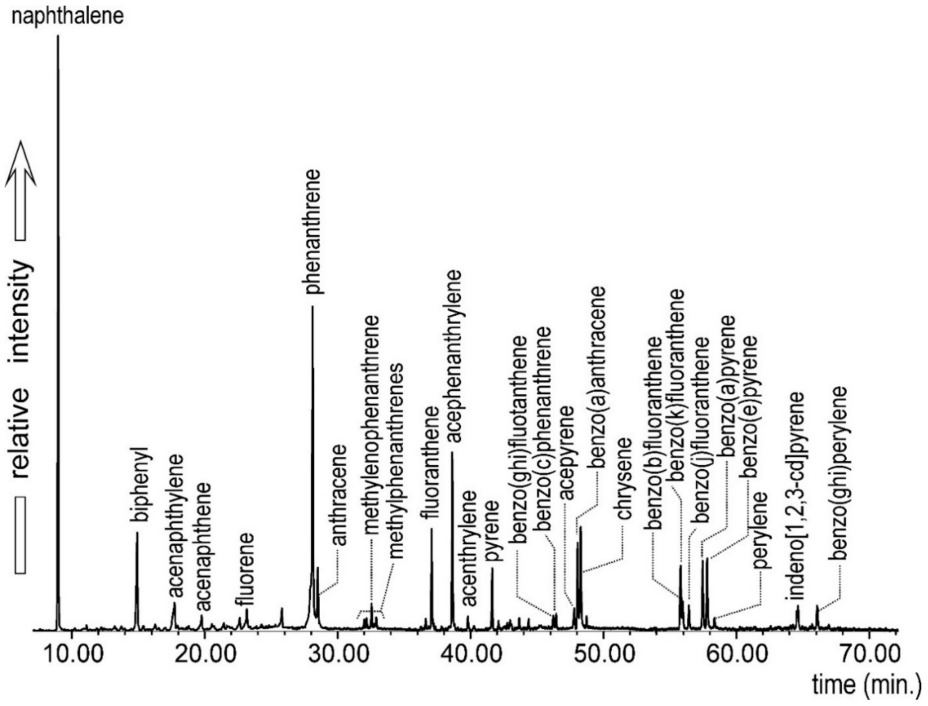

Figure 2. Generalized PAH distribution in charcoal extract (sample W7).

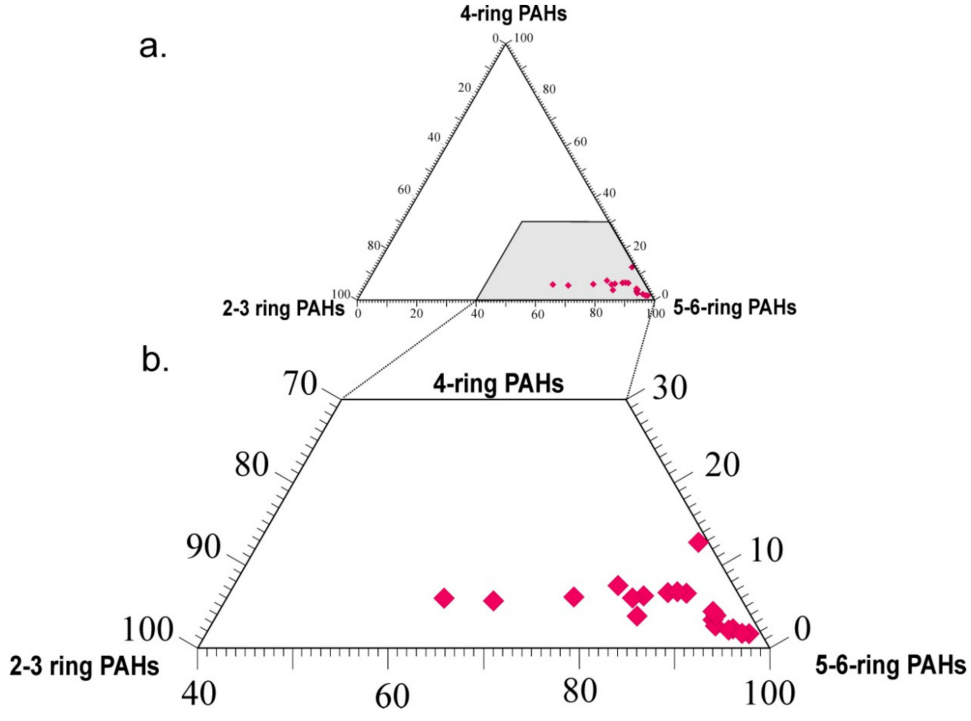

Figure 3. Distribution of PAHs according to the number of rings in a molecule, (**a**). general ternary diagram showing 5–6 ring PAHs predominance, (**b**). A truncated ternary diagram with detailed PAHs distribution.

The four types of PAHs distribution can be distinguished within the sample set as shown in Figure 4, (i) with the increased content of lighter 2–4 ring PAHs, with the increased content of lighter 2–4 ring PAHs, Light/Heavy PAHs ratio 0.15–0.31 (samples W1, W3, W5, W9, W12, and W18), (ii) with very low content of lighter PAHs, Light/Heavy PAHs ratio 0.01–0.06 (W11, W13, 15, W17, W19, W21, and W22), (iii) with benzofluoranthenes (Bf) dominating over

benzopyrenes (Bp), with ∑Bf/∑Bp ratio >1.0 (W1, W3, W5, W6, W8, and W17 samples and (iiii) benzopyrenes dominating over benzofluoranthenes, with ∑Bf/∑Bp ratio >1.0.

Table 6. Polycyclic aromatic hydrocarbon concentrations in charcoals investigated (ppm).

Sample	N	Bi	Ace	Acy	F	P	A	MeP	Fl	Acen	AcPhe	Py	BcPhe
W1	0.16	4.84	0.58	-	0.34	4.34	3.93	-	1.39	0.07	0.14	0.80	0.07
W2	0.04	1.55	-	-	0.23	0.71	0.07	-	0.40	0.01	0.05	0.20	0.02
W3	0.40	0.13	-	-	0.13	0.65	0.10	-	0.40	-	-	0.30	-
W4	0.09	-	-	-	-	0.53	0.06	-	0.25	0.02	0.04	0.20	0.01
W5	0.47	8.93	0.15	0.85	0.20	1.25	0.16	0.19	1.00	0.06	0.09	0.63	0.06
W6	29.21	12.08	0.12	-	-	20.89	1.50	-	36.89	1.45	2.38	26.33	1.30
W7	1.43	1.56	0.64	0.92	-	5.45	0.70	-	4.66	0.49	0.54	3.37	0.27
W8	21.96	6.56	0.28	-	1.51	19.09	3.05	5.13	16.84	0.62	0.67	11.96	0.66
W9	0.19	0.67	0.04	0.07	-	5.00	0.99	-	2.13	0.09	0.17	1.77	0.10
W10	12.45	2.53	0.05	1.40	-	2.49	0.30	-	3.22	-	0.17	1.65	0.15
W11	-	-	-	-	-	0.13	0.03	-	0.23	-	0.01	0.06	-
W12	6.78	3.09	0.19	2.17	0.18	7.01	0.94	0.86	5.51	0.22	0.38	3.59	0.25
W13	1.79	1.59	-	-	0.14	3.00	0.44	0.15	2.49	0.17	0.21	1.97	0.21
W14	7.92	3.34	0.28	4.01	1.91	11.00	1.47	2.23	12.48	0.47	0.87	7.95	0.45
W15	50.20	9.29	0.14	0.74	0.05	32.46	5.43	3.44	19.79	0.82	0.92	16.63	2.03
W16	-	-	-	-	-	-	-	-	-	-	-	-	-
W17	-	0.20	-	-	-	0.23	0.08	-	0.23	-	0.03	0.14	-
W18	-	0.22	-	-	-	0.71	0.19	-	24.95	-	0.05	0.36	0.07
W19	-	0.41	0.08	-	-	0.59	0.11	-	0.54	-	0.04	0.50	0.16
W20	-	-	-	-	-	-	-	-	-	-	-	-	-
W21	0.85	-	-	-	0.20	4.93	1.21	0.83	4.27	-	-	3.17	0.31
W22	0.86	1.52	-	-	0.14	0.60	0.10	-	0.45	-	-	0.36	0.08
W23	-	-	-	-	-	0.72	0.14	-	0.48	-	-	0.30	0.03
W24	-	-	-	-	-	-	-	-	-	-	-	-	-
W25	-	-	-	-	-	-	-	-	-	-	-	-	-
W26	-	-	9.37	-	0.13	6.35	1.09	0.55	9.26	-	0.31	5.68	-
W27	-	-	-	-	-	-	-	-	-	-	-	-	-
W28	-	-	0.06	-	-	0.52	0.13	-	0.77	-	-	0.46	-
W29	-	-	-	-	-	-	-	-	-	-	-	-	-
W30	-	-	0.44	-	0.22	1.80	0.31	-	1.80	-	-	1.26	-
W31	-	-	-	-	-	-	-	-	-	-	-	-	-

Sample	BaA	Ch	BghiFl	AcPy	BbF	BkF	BaF	BaP	BeP	Pe	IP	BghiP
W1	0.18	0.15	0.04	0.10	11.82	3.77	4.29	9.10	3.86	2.70	0.53	0.17
W2	0.11	0.02	-	-	3.75	2.13	0.12	7.99	3.46	0.74	-	-
W3	-	-	-	-	4.35	2.22	0.07	2.07	1.71	-	-	-
W4	0.11	0.01	0.03	0.05	3.69	1.10	0.06	4.55	2.77	2.22	-	-
W5	0.20	0.03	0.03	0.03	7.99	3.82	0.25	3.36	4.41	3.87	-	-
W6	4.27	2.38	2.65	1.34	436.61	105.04	-	166.29	223.62	48.16	30.88	3.08
W7	1.35	0.65	0.30	-	68.46	15.93	1.38	51.46	36.62	9.51	6.29	0.83
W8	4.23	1.41	0.85	0.16	206.13	51.88	3.79	109.38	120.13	41.67	10.17	1.75
W9	0.52	0.28	0.09	0.13	17.97	6.20	0.68	21.99	17.52	3.49	-	-
W10	0.23	0.09	0.18	0.06	23.69	10.10	0.62	23.65	20.08	6.90	1.17	0.18
W11	-	-	-	-	3.22	1.34	0.03	5.05	3.04	1.92	-	-
W12	1.03	0.50	0.38	0.27	47.56	6.43	0.97	36.84	29.28	5.52	3.46	0.32
W13	1.10	0.58	0.12	0.10	53.07	8.62	1.07	38.63	37.74	8.80	7.70	0.71
W14	1.88	0.72	0.68	0.25	118.37	21.36	2.14	73.62	81.47	24.65	8.43	0.99
W15	17.67	6.04	0.75	-	928.50	335.67	24.53	892.60	1037.38	140.52	23.35	5.16
W16	-	-	-	-	-	-	-	-	-	-	-	-
W17	-	-	-	-	5.09	2.28	0.06	2.03	2.18	-	-	-
W18	0.15	0.09	-	-	44.25	28.35	0.89	35.53	50.92	5.78	-	-
W19	0.46	0.13	0.26	0.07	25.85	7.79	0.64	27.42	50.99	7.41	7.69	-
W20	-	-	-	-	-	-	-	-	-	-	-	-
W21	1.87	0.69	0.24	-	60.50	38.64	2.09	64.04	59.01	14.65	0.89	0.07
W22	0.56	0.09	-	-	10.14	4.08	0.22	14.98	28.74	8.77	1.35	0.30
W23	0.09	0.02	-	-	7.85	0.00	0.12	6.32	1.98	2.63	-	-
W24	-	-	-	-	-	-	-	-	0.00	0.00	-	-
W25	-	-	-	-	-	-	-	-	0.00	0.00	-	-
W26	-	-	0.45	-	93.48	78.41	3.25	99.26	113.43	21.14	-	-
W27	-	-	-	-	-	-	0.00	-	0.00	-	-	-
W28	-	-	-	-	3.70	5.19	0.45	7.32	4.92	4.78	-	-
W29	-	-	-	-	-	-	-	-	0.00	0.00	-	-
W30	-	-	0.12	-	14.65	8.69	1.13	35.31	14.44	8.62	-	-
W31	-	-	-	-	-	-	-	-	-	-	-	-

N—naphthalene, Bi—biphenyl, Ace—acenaphene, Acy—acenaphthylene, F—fluorene, P—phenanthrene, A—anthracene, MeP—methylenephenanthrene, Fl—fluoranthene, Acen—acenthrylene, AcPhe—acephenanthrylene, Py—pyrene, BcPhe—benzo(c)phenanthrene, BaA benzo(a)anthracene, Ch—chrysene, BghiFl—benzo(ghi)fluoranthene, AcPy—acepyrene, BbF—benzo(b)fluoranthene, BkF—benzo(k)fluoranthene, BaF—benzo(a)fluoranthene, BaP—benzo(a)pyrene, BeP—benzo(e)pyrene, Pe—perylene, IP—indeno(1,2,3-cd)pyrene, BghiP—benzo(ghi)perylene.

Table 7. Values of diagnostic PAH ratios for the charcoals investigated.

Sample	P/A	A/(A + P)	Fl/(Fl + Py)	Fl/Py	Fl/(Fl + P)	BaA/(BaA + Ch)	BaP/BghiP	IP/BghiP	IP/(IP + BghiP)	BaA/BaP	Py/BaP
W1	1.10	0.48	0.64	1.74	0.24	0.55	52.52	3.05	0.75	0.02	0.09
W2	10.48	0.09	0.67	2.04	0.36	0.86	-	-	-	0.01	0.02
W3	6.17	0.14	0.58	1.36	0.38	-	-	-	-	0.00	0.14
W4	9.01	0.10	0.56	1.25	0.32	0.95	-	-	-	0.02	0.04
W5	7.96	0.11	0.61	1.58	0.44	0.89	-	-	-	0.06	0.19
W6	13.95	0.07	0.58	1.40	0.64	0.64	54.04	10.03	0.91	0.03	0.16
W7	7.83	0.11	0.58	1.38	0.46	0.68	61.77	7.55	0.88	0.03	0.07
W8	6.26	0.14	0.58	1.41	0.47	0.75	62.36	5.80	0.85	0.04	0.11
W9	5.06	0.16	0.55	1.21	0.30	0.65	-	-	-	0.02	0.08
W10	8.38	0.11	0.66	1.95	0.56	0.73	130.97	6.47	0.87	0.01	0.07
W11	4.71	0.18	0.78	3.61	0.64	-	-	-	-	0.00	0.01
W12	7.44	0.12	0.61	1.54	0.44	0.67	115.20	10.81	0.92	0.03	0.10
W13	6.79	0.13	0.56	1.26	0.45	0.66	54.28	10.82	0.92	0.03	0.05
W14	7.46	0.12	0.61	1.57	0.53	0.72	74.01	8.47	0.89	0.03	0.11
W15	5.98	0.14	0.54	1.19	0.38	0.75	172.93	4.52	0.82	0.02	0.02
W16	-	-	-	-	-	-	-	-	-	-	-
W17	2.89	0.26	0.63	1.70	0.50	-	-	-	-	0.00	0.07
W18	3.78	0.21	0.99	69.87	0.97	0.64	-	-	-	0.00	0.01
W19	5.60	0.15	0.52	1.08	0.48	0.78	-	-	1.00	0.02	0.02
W20	-	-	-	-	-	-	-	-	-	-	-
W21	4.08	0.20	0.57	1.35	0.46	0.73	955.55	13.31	0.93	0.03	0.05
W22	6.15	0.14	0.56	1.25	0.43	0.86	49.82	4.49	0.82	0.04	0.02
W23	5.16	0.16	0.61	1.58	0.40	0.79	-	-	-	0.01	0.05
W24	-	-	-	-	-	-	-	-	-	-	-
W25	-	-	-	-	-	-	-	-	-	-	-
W26	5.80	0.15	0.62	1.63	0.59	-	-	-	-	0.00	0.06
W27	-	-	-	-	-	-	-	-	-	-	-
W28	3.95	0.20	0.62	1.66	0.59	-	-	-	-	0.00	0.06
W29	-	-	-	-	-	-	-	-	-	-	-
W30	5.91	0.14	0.59	1.43	0.50	-	-	-	-	0.00	0.04
W31	-	-	-	-	-	-	-	-	-	-	-

P—phenanthrene, A—anthracene, Fl—fluoranthene, Py—pyrene, BaA—benzo(a)anthracene, Ch—chrysene, BaP—benzo(a)pyrene, BeP—benzo(e)pyrene, Pe—perylene, IP—indeno(1,2,3-cd)pyrene, BghiP—benzo(ghi)perylene.

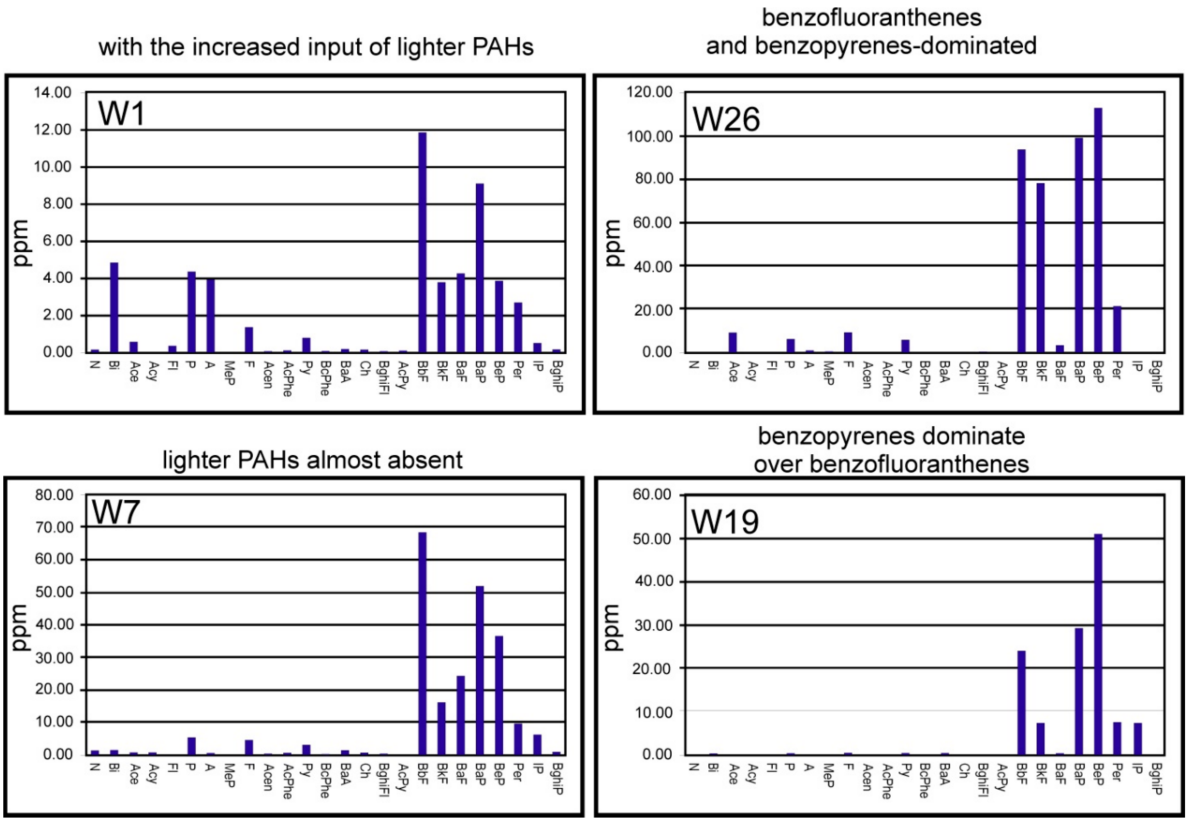

Figure 4. Distribution types of PAHs in charcoal extracts.

Several PAH diagnostic ratios were calculated based on quantitative analysis [30,31] (Table 7). On the PAH diagnostic diagrams of the Fl/(Fl + Py) ratio over the A/(A + P), BaA/(Ch + BaA), and P/(IP + BghiPer) ratios (Figure 4), all samples group closely with

each other in the area corresponding to "biomass and coal combustion". This is directly related to the charcoal origin as the product of biomass pyrolysis, although the process occurs with limited oxygen access and cannot be considered combustion in the proper term meaning. The W1, W11, and W18 samples showed extreme diagnostic ratios, and they did not fit the whole sample set (Figure 5).

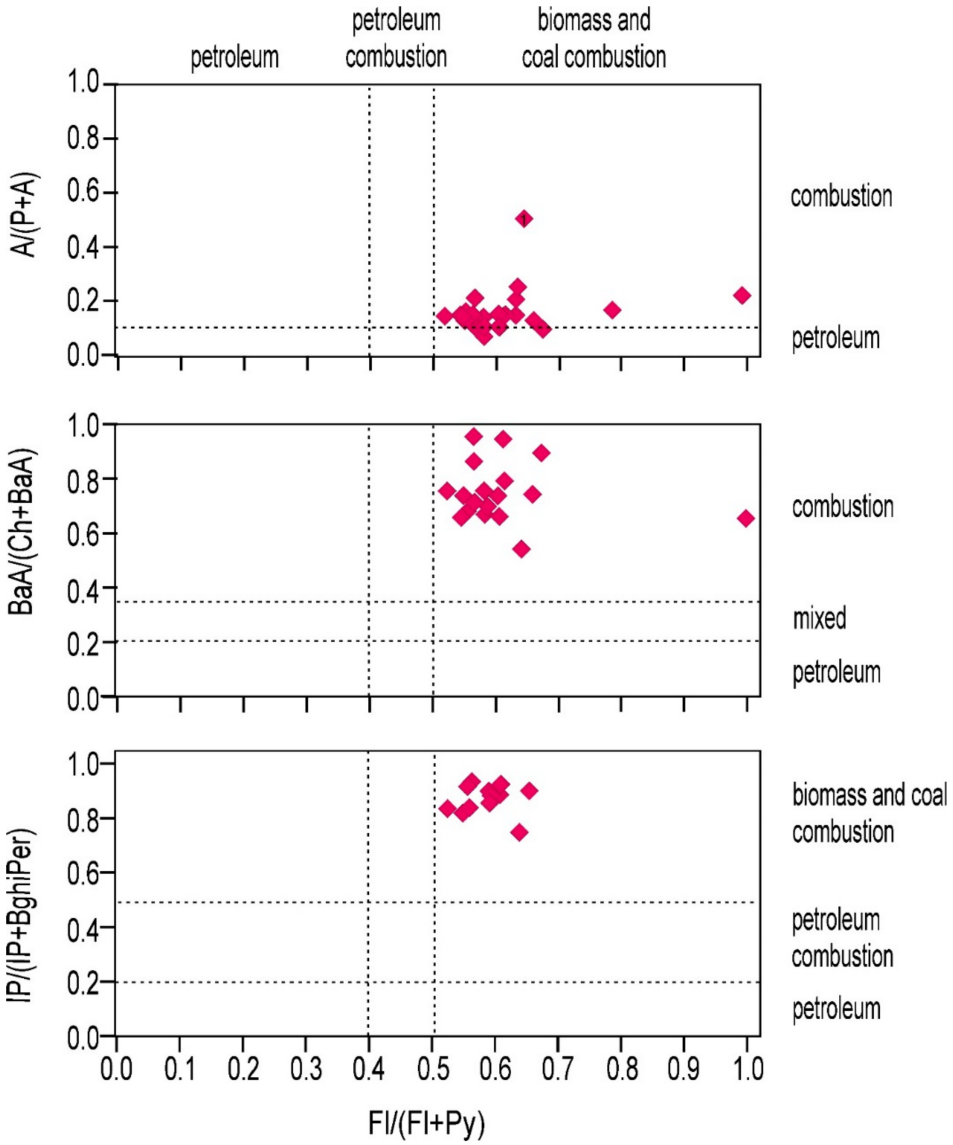

Figure 5. Diagnostics diagrams of PAHs in charcoals investigated [15]. A—anthracene, P—phenanthrene, Fl—fluoranthene, Py—pyrene, BaA—benzo(a)anthracene, Ch—chrysene, IP—indeno(1,2,3-cd)pyrene, BghiP—benzo(ghi)perylene.

4. Discussion

Taking into account the degree of risk to the environment and, above all, to human health, the toxic elements determined in charcoal during the analysis were divided into four groups [21–23]:

1. Potentially very highly harmful elements: As, Cd, Cu, Hg, and Pb.
2. Potentially highly harmful elements: Zn, Ba, Cr, Mn, and Mo.
3. Elements representing a lesser degree of a hazard: Co, Ni, Sn, and Te.
4. Elements representing a low degree of a hazard: Ag, Bi, Ce, Se, Sr, and Zr.

The contamination of charcoal with heavy metals and other toxic elements may cause their penetration into the natural environment and the human body. Skin contact with the tested grill fuel and the inhalation of coal dust occur at every stage of charcoal use, from production to use. Up to now, no studies have been conducted to what extent toxic elements are absorbed by living organisms from charcoal. However, the literature about toxic elements occurrence in other fuels together with elements health and environmental impact is quite extensive [32,33].

Toxic metal occurrence in charcoal, in particular heavy metals, is largely caused by their presence in starting material for its production, i.e., it is related to the penetration of these elements into the wood from the soil during the tree's life cycle [34]. Additional contamination may also result from technological processes, and above all, the equipment and tools used during the thermal treatment of wood. For example, old-type retorts are made of galvanized and copper plates, whereas the newer retorts—of steel plates. This type of material may contribute to charcoal contamination with heavy metals.

The sum of PAH concentrations in the charcoal samples investigated shows high variability in the range of 12.55–3554.11 ng/g charcoal. In samples W16, W20, W27, W29, and W31, PAHs were absent or below a detection limit. The highest content of the PAHs sum was in the W15 and W6 samples, 3554.11 and 1156.47 ng/g of charcoal, respectively. The sample set can be divided into three subsets: (i) with the highest ∑PAH concentrations >200 ng/g of charcoal comprising the W6, W7, W8, W14, W15, W21, and W26 samples (7 samples), (ii) with intermediate ∑PAH concentrations in the range of 100–200 ng/g comprising the W10, W12, W13, W18, and W19 (5 samples), and (iii) with the lowest PAH concentrations being <100 ng/g comprising the W1–5, W9, W11, W17, W22, W23, W28, and W30 samples (12 samples) (Table 8).

To assess charcoal health and the environmental impact, several indicators were calculated. They defined the toxicity of individual PAHs and the whole compound group as well to assess the risk caused by exposure to a PAH mixture. In this approach, BaP is considered to be a reference compound. The carcinogenic potential, called the toxicity equivalence factor (TEF), of other PAHs is calculated relative to BaP for 16 PAHs according to the EPA list. The toxicity equivalent value (TEQ) is the sum of individual PAH concentrations and their relative toxicity coefficients [35] (Table 8). Such an approach is required since the carcinogenicity of individual PAHs depends on their molecular structure, which determines the biological activity of the compound. The organization of carbon atoms as a bay region causes a high degree of biochemical reactivity to some PAHs and their metabolites [36].

The mutagenicity equivalent (MEQ) was given as the sum of 16 individual PAH concentrations and their relative mutagenicity coefficients [18]. In this approach, only unsubstituted parent PAHs are considered since pyrogenic PAHs (produced under the influence of high heat) are dominated by these compounds with a slope distribution of C0 > C1 > C2 > C3 > C4 of alkylated derivatives. Petrogenic sources (mainly crude oil, coals, and similar materials) are rich in alkyl-substituted PAHs.

The TEQ and MEQ values vary considerably, since they depend on the contents of PAHs with high TEF toxicity ratios. The W15 and W6 charcoal showed the highest values: 1023.87 and 984.98 for W15 and 224.43 and 202.78, respectively (Table 8). The lowest values were found for the W3 and W17 samples, ca. 2.60 for both parameters. The averages were 66.12 and 66.30, respectively. These values suggest considerable risk for cancer and mutation caused by close contact with charcoals, both dermal and by inhalation. Comparable values of TEQ and MEQ for soot containing PAHs derived from combustion of various solid fuels, such as pellets and hard coal, do not exceed 160 and 95, respectively [17].

A ratio of carcinogenic PAHs., i.e., BaA, Ch, BbF, BkF, BaP, IP, and DBA, to a sum of all PAHs (∑PAHcarc/∑PAHtot in Table 8) expresses carcinogenicity of charcoal; the closer value to 1.0 the higher carcinogenicity [18,37,38]. In the investigated charcoals, the values of this ratio are 0.80 on average, with 15 samples, i.e., 50% of the set, exceeding these average values. The W15 and W17 samples show ∑PAHcarc/∑PAHtot above 0.90

(0.90 and 0.94, respectively). Even the lowest ∑PAHcarc/∑PAHtot value is 0.59 (W1). This indicates the high carcinogenicity of the charcoals investigated.

Table 8. Indices assessing possible health and environmental impact of charcoal investigated.

Sample	∑Bf/∑Bp (1)	PAH Sum (2)	TEQ (3)	$\sum PAH_{carc}/\sum PAH_{tot}$ (4)	BaPE (5)	BaPE/BaP (6)	MEQ (7)	L/H (8)
W1	1.53	53.37	10.79	0.59	10.35	1.14	10.24	0.45
W2	0.52	21.61	8.59	0.87	8.41	1.05	8.52	0.18
W3	1.76	12.55	2.73	0.83	2.53	1.22	2.63	0.20
W4	0.66	15.79	5.04	0.77	4.89	1.08	4.83	0.08
W5	1.55	38.03	4.57	0.68	4.20	1.25	4.32	0.58
W6	1.39	1156.47	224.43	0.82	208.78	1.26	202.78	0.13
W7	0.97	212.81	60.77	0.82	58.45	1.14	57.57	0.10
W8	1.14	639.88	136.91	0.78	129.56	1.18	125.90	0.16
W9	0.63	80.08	24.48	0.81	23.71	1.08	23.55	0.16
W10	0.79	111.34	27.21	0.71	26.23	1.11	26.57	0.28
W11	0.57	15.06	5.51	0.84	5.37	1.06	5.38	0.03
W12	0.83	163.71	42.76	0.76	41.15	1.12	39.59	0.23
W13	0.82	170.40	45.77	0.82	44.06	1.14	43.32	0.08
W14	0.91	388.91	88.79	0.77	84.79	1.15	81.79	0.16
W15	0.67	3554.11	1023.87	0.90	987.11	1.11	984.98	0.04
W16	-	-	-	-	-	-	-	-
W17	1.77	12.55	2.77	0.94	2.54	1.25	2.60	0.08
W18	0.85	192.50	42.83	0.83	40.62	1.14	42.62	0.16
W19	0.44	131.15	31.61	0.86	30.42	1.11	31.76	0.02
W20	-	-	-	-	-	-	-	-
W21	0.82	258.47	74.27	0.86	71.20	1.11	74.02	0.06
W22	0.33	73.34	16.63	0.81	16.30	1.09	16.48	0.06
W23	0.96	20.68	7.12	0.78	6.87	1.09	6.32	0.09
W24	-	-	-	-	-	-	-	-
W25	-	-	-	-	-	-	-	-
W26	0.82	442.16	116.49	0.87	111.29	1.12	118.86	0.08
W27	-	-	-	-	-	-	-	-
W28	0.76	28.31	8.21	0.75	7.94	1.09	8.62	0.07
W29	-	-	-	-	-	-	-	-
W30	0.49	88.79	37.65	0.82	36.94	1.05	37.48	0.07
W31	-	-	-	-	-	-	-	-

BaPeq was used to evaluate the toxicity of PAHs (Table 8). This method is typically employed by researchers to estimate the BaPeq toxicity of different PAHs in air, soil, and street dust [16,39]. The ratio values varied considerably from 2.53 (W3) to 987.11 (W15). The highest level corresponds to that found in the carbon black manufacturing industry [40] and indicates a serious occupational risk in workers caused by exposure to charcoals. The inhalation of charcoal dust may lead to lung cancer, but direct contact with it will cause various forms of skin cancers.

There is no significant correlation between the method of charcoal production, wood type, and carcinogenicity of the final product.

Contaminants found in charcoal derive from a few sources. PAHs originate from the process of wood pyrolysis that, under low-oxygen conditions, produces both tar and charcoal. When the separation of these products from each other is poor, the final commercial product—charcoal—will contain high concentrations of PAHs. The wood type is insignificant in this case since biologically similar material is applied, i.e., deciduous trees such as beech or oak.

5. Conclusions

Charcoal samples were investigated to determine their health and environmental impact. It was found that all samples were contaminated with elements representing a

very high degree of hazard (e.g., Cu), a high degree of hazard (Ba and Mn), and a medium degree of hazard (Sr). In the group of elements with a very high degree of toxicity, their sum in seventeen samples was above 2 ppm. The four elements representing a high degree of hazard exceeded 500 ppm in total in each sample. The elements representing a medium degree of hazard exceeded the level of 2 ppm in the next 17 samples. The group of elements representing the lowest degree of hazard, represented by only four elements, exceeded the total level of 100 ppm. The concentrations of Cu, Ba, Mn, and Sr exceeded 100% up to (in extreme cases) 2100% of the lowest acceptable safe concentrations. In addition, Zr, Ag, Se, As, Cd, and Zn occasionally exceeded acceptable values. The remaining elements, including Cr, Mo, Hg, Te, Sn, Ce, Pb, Bi, and Co, were present in trace amounts in the charcoal. The proven presence of toxic elements should be of interest to people involved in the production, transport, and handling of charcoal. While users of this product have short-term contact with charcoal during grilling, the employees professionally involved in the production of this fuel exceed the daily norms of inhalation and skin contact with individual carcinogenic elements. Therefore, the authors hope to draw attention to the problems related to the relationship of the grill fuel composition and the safety of its use. It seems that the application of basic protection measures, i.e., gloves and masks, will be sufficient to protect the human body against harmful elements.

Given the health risk assessment for the individual carcinogenic elements, the risk of developing cancer or other health problems is high. All charcoals showed a high carcinogenicity level caused by both PAH and carcinogenic metal occurrence, i.e., Cu, Ba, Sr, and Mn. Since $\sum$PAHcarc/$\sum$PAHtot was close to 1, together with high TEQ and MEQ values, the contact of workers with charcoal should be limited as much as possible during all production operations and packaging. Prolonged exposure to charcoal and charcoal dust containing large quantities might cause the health problems mentioned above. This applies to employees actively involved in the production and transport of charcoal and, to a lesser extent, to users of this fuel.

Individual protection means are required as well as procedures limiting dermal contact and charcoal dusting to decrease charcoal particle inhalation, i.e., lung cancer risk. The key step is to work out and introduce suitable norms for charcoal production and product control, considering the health risk to employees and future users. Whereas there are numerous regulations concerning contact with toxic metals, there are no, to our knowledge, regulations concerning exposure to PAHs in charcoal. In particular, a means should be undertaken to decrease the tar content in the final product since the tar is the PAH-bearing medium. Since users are mostly exposed to evaporating PAHs during the first stage of charcoal burning at relatively low temperatures, a suitable warning should be given at the charcoal packages against smoke/dust inhalation.

Moreover, there is a high variability of toxic metal contents, PAH concentrations, and values of indices assessing possible health impacts together with no clear relationship between their values for charcoal and the method of charcoal production. This suggests that every producer/charcoal batch should be analyzed for contaminant content. The presence of contaminants results from the combination of a few factors, i.e., the material itself, the production method (PAHs), or a retort.

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